(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 April 2005 (07.04.2005)

PCT

(10) International Publication Number
WO 2005/030858 A2

(51) International Patent Classification[7]: C08K 9/00

(21) International Application Number: PCT/US2004/019769

(22) International Filing Date: 21 June 2004 (21.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/480,348 20 June 2003 (20.06.2003) US

(71) Applicants *(for all designated States except US)*: **WILLIAM MARSH RICE UNIVERSITY** [US/US]; 6100 Main Street, Houston, TX 77843 (US). **UNIVERSITY OF HOUSTON** [US/US]; 4800 Calhoun Street, Houston, TX 77204-2015 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **TOUR, James, M.** [US/US]; 4625 Spruce Street, Bellaire, TX 77401 (US). **HUDSON, Jared, L.** [US/US]; 1737 Sunset Blvd., No. 22, Houston, TX 77005 (US). **KRISHNAMOORTI, Ramanan** [IN/US]; 4954 Willow St., Bellaire, TX 77401 (US). **YURELKI, Koray** [TR/US]; 4400 Memorial Dr., No. 2169, Houston, TX 77007 (US). **MITCHELL, Cynthia, A.** [US/US]; 904 Westcott, No. 303, Houston, TX 77007 (US).

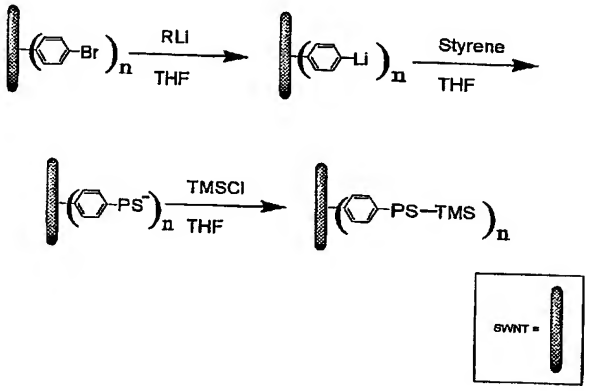
(74) Agents: **GARSSON, Ross, Spencer** et al.; WINSTEAD SECHREST & MINICK P.C., P.O. Box 50784, Dallas, TX 75201-0784 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: POLYMERIZATION INITIATED AT THE SIDEWALLS OF CARBON NANOTUBES



(57) Abstract: The present invention is directed to aryl halide (such as aryl bromide) functionalized carbon nanotubes can be utilized in anionic polymerization processes to form polymer-carbon nanotube materials with improved dispersion ability in polymer matrices. In this process the aryl halide is reacted with an alkyllithium species or is reacted with a metal to replace the aryl-bromine bond with an aryl-lithium or aryl-metal bond, respectively. It has further been discovered that other functionalized carbon nanotubes, after deprotonation with a deprotonation agent, can similarly be utilized in anionic polymerization processes to form polymer-carbon nanotube materials. Additionally or alternatively, a ring opening polymerization process can be performed. The resultant materials can be used by themselves due to their enhanced strength and reinforcement ability when compared to their unbound polymer analogs. Additionally, these materials can also be blended with pre-formed polymers to establish compatibility and enhanced dispersion of nanotubes in otherwise hard to disperse matrices resulting in significantly improved material properties. The resultant polymer-carbon nanotube materials can also be used in drug delivery processes due to their improved dispersion ability and biodegradability, and can also be used for scaffolding to promote cellular growth of tissue.

WO 2005/030858 A2

European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 April 2005 (07.04.2005)

PCT

(10) International Publication Number
WO 2005/030858 A3

(51) International Patent Classification[7]: C08K 7/24, 3/04, 7/06, C01B 31/02, C08F 292/00

(21) International Application Number: PCT/US2004/019769

(22) International Filing Date: 21 June 2004 (21.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/480,348 20 June 2003 (20.06.2003) US

(71) Applicants *(for all designated States except US)*: **WILLIAM MARSH RICE UNIVERSITY** [US/US]; 6100 Main Street, Houston, TX 77843 (US). **UNIVERSITY OF HOUSTON** [US/US]; 4800 Calhoun Street, Houston, TX 77204-2015 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **TOUR, James, M.** [US/US]; 4625 Spruce Street, Bellaire, TX 77401 (US). **HUDSON, Jared, L.** [US/US]; 1737 Sunset Blvd., No. 22, Houston, TX 77005 (US). **KRISHNAMOORTI, Ramanan** [IN/US]; 4954 Willow St., Bellaire, TX 77401 (US). **YURELKI, Koray** [TR/US]; 4400 Memorial Dr., No. 2169, Houston, TX 77007 (US). **MITCHELL, Cynthia, A.** [US/US]; 904 Westcott, No. 303, Houston, TX 77007 (US).

(74) Agents: **GARSSON, Ross, Spencer** et al.; WINSTEAD SECHREST & MINICK P.C., P.O. Box 50784, Dallas, TX 75201-0784 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

(88) Date of publication of the international search report: 23 June 2005

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/030858 A3

(54) Title: POLYMERIZATION INITIATED AT THE SIDEWALLS OF CARBON NANOTUBES

(57) Abstract: The present invention is directed to aryl halide (such as aryl bromide) functionalized carbon nanotubes can be utilized in anionic polymerization processes to form polymer-carbon nanotube materials with improved dispersion ability in polymer matrices. In this process the aryl halide is reacted with an alkyllithium species or is reacted with a metal to replace the aryl-bromine bond with an aryl-lithium or aryl-metal bond, respectively. It has further been discovered that other functionalized carbon nanotubes, after deprotonation with a deprotonation agent, can similarly be utilized in anionic polymerization processes to form polymer-carbon nanotube materials. Additionally or alternatively, a ring opening polymerization process can be performed. The resultant materials can be used by themselves due to their enhanced strength and reinforcement ability when compared to their unbound polymer analogs. Additionally, these materials can also be blended with pre-formed polymers to establish compatibility and enhanced dispersion of nanotubes in otherwise hard to disperse matrices resulting in significantly improved material properties. The resultant polymer-carbon nanotube materials can also be used in drug delivery processes due to their improved dispersion ability and biodegradability, and can also be used for scaffolding to promote cellular growth of tissue.